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UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mmho	millimho
cm	centimeter	mmho/cm	millimho per centimeter
g/L	gram per liter	mV	millivolt
h	hour	mV/s	millivolt per second
in	inch	nA	nanoampere
L	liter	nA/cm^2	nanoampere per square centimeter
mg	milligram	pct	percent
$mg/cm^2 \cdot h$	milligram per square centimeter per hour	ton/d	ton per day
mpy	mil per year	V	volt
mL	milliliter	V/decade	volt per decade
µm	micrometer	vol pct	volume percent
µm/h	micrometer per hour	W	watt

CORROSION RATES OF GRINDING MEDIA IN MILL WATER

By W. K. Tolley,[1] I. L. Nichols,[2] and J. L. Huiatt[3]

ABSTRACT

This report presents data collected during research by the Bureau of Mines on corrosion of grinding media. Corrosion rates of eight alloys commonly used in grinding media were tested in synthetic mill water using an ultrasonic grinding device especially designed for this work. Electrochemical measurements showed variations in corrosion rates for these alloys between 9.8 mpy for medium-carbon steels and 0.14 mpy for high-chromium white irons.

Bureau data are discussed along with data from the literature to indicate that corrosion causes less than 10 pct of the wear of grinding media in commercial grinding mills. A comparison of corrosion rates for various types of grinding media shows that alloying elements and electrochemically active inclusions in steel affect the corrosion behavior of the media.

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INTRODUCTION

While grinding is unavoidable in nearly all mineral processing, it is an inefficient and costly step. As an example, the National Academy of Sciences (NAS) (4)[4] estimates that the copper industry consumed 205,000 tons of grinding media in 1978. A typical copper producer processing 100,000 tons of ore per day may spend approximately $25,000 daily to replace media consumed just in ball milling. Similarly, the iron industry consumed approximately 708,000 tons of grinding media to produce pellets in 1978. The Bureau of Mines is investigating the corrosion of grinding media to identify the chemical and electrochemical factors that influence this corrosion and to determine the extent to which corrosion contributes to consumption of the media. This report presents data from the initial phase of this continuing study, and compares original results with data on commercial mill wear rates reported in the literature.

Grinding medium wear is believed to result from complex and poorly understood interactions among corrosion, abrasion, and impact. The contribution from each of these three mechanisms has not been firmly established, owing in part to the difficulty of measuring the separate components, and conflicting views are found throughout the literature on the relative importance of each mechanism. To serve as a basis for more detailed studies, a grinding mill simulator was adopted to abrade a test specimen while measuring its corrosion rate. The method uses ultrasonic abrasion to scour the surface of the specimen. The scouring occurs uniformly across the surface of the test specimen to allow accurate determination of the corroding area. Other methods for abrading the surface, such as scratching with a stylus, give unknown test areas. Wright (21) showed that ultrasonic scouring could produce significant abrasion during corrosion testing.

Since no data are available on the extent of alloy passivation in a commercial mill, no attempt was made in this phase of the study to measure passivation or its effect on medium corrosion, as would be done in a basic corrosion study. Rather, the ultrasonic device was used as a simple model of a practical mill. Hence, the data from this initial phase of research should not necessarily be viewed as generically applicable information on fundamental corrosion behavior.

PREVIOUS GRINDING MEDIUM CORROSION STUDIES

Ellis (6) performed early work on the wear of grinding media. He noted that when oxygen was present in the mill, wear of carbon steels increased dramatically compared with tests when oxygen was excluded. He also found that carbon steels wore at the same rate as stainless alloys (i.e., alloys containing more than 15 pct Cr) when oxygen was absent from the mill. His data suggested that between 50 and 75 pct of the wear of low-chromium grinding alloys in laboratory mills was caused by corrosion. His data also showed that grinding efficiency decreased as the amount of corrosion of the medium increased.

Bond measured energy consumption and corresponding wear rates of grinding media (1). He concluded that medium wear was about 5 to 10 times greater in wet grinding than in dry grinding. He suggested that this increase in wear was the result of corrosion in wet grinding operations, since grinding constantly scours the medium to maintain fresh, chemically active surfaces. These active surfaces, he reasoned, would readily corrode during contact with the grinding solution. He further proposed (2) that galvanic corrosion could contribute to wear owing to differences in electrochemical potential between the metal and the slurry.

More recently, Hoey (8) and Lui (9-10) studied the corrosion of grinding media in various mineral slurries. They used inhibitors to reduce the corrosion component of wear in laboratory mills. The corrosion rate of the media was found to be a function of the mineral in the slurry. For copper ore grinding, the corrosion of white irons was found to be between about 40 and 60 pct of the wear. Corrosion was about 25 to 35 pct of the wear for the same media when grinding iron ores. They also measured the corrosion potentials of the steel grinding balls to assure that passivation of the media was not occurring in the grinding tests and concluded that the iron ore was more abrasive than the sulfide ore, which resulted in higher abrasion of the steel surface and therefore a reduced proportion of the wear caused by corrosion.

Remark (16) tested inhibitors to reduce galvanic corrosion currents of grinding media and concluded that appropriate inhibitors could prevent about 75 pct of this corrosion loss. He assumed galvanic corrosion to be the major factor causing medium wear in grinding mills. Based on theoretical estimates of corrosion potentials in an operating mill, he estimated 40 to 90 pct of medium wear to be a result of corrosion. These values contradict reports by Natarajan (14), who concluded based upon electrochemical tests that in grinding taconite corrosion causes only a small portion of the medium wear. His data also indicated that galvanic corrosion occurs between minerals and media in a grinding mill.

ELECTROCHEMICAL CORROSION MEASUREMENT TECHNIQUES

Electrochemical techniques have been used extensively to measure corrosion rates in aqueous media. Typically, material to be tested is connected to a potentiostat, which measures the corrosion current from the test piece while controlling the electrical potential of the material. The material to be tested is suspended in the test solution between two inert electrodes, generally made of either platinum or graphite. A capillary tube, which acts as a salt bridge, is placed adjacent to the test surface and connected to a reference electrode, generally a saturated calomel electrode (SCE). During testing, the potentiostat maintains the electrochemical potential of test material at a programmed value relative to the reference electrode by applying a potential to inert or auxiliary

[4]Underlined numbers in parentheses refer to items in the list of references preceding the appendixes.

electrodes. The current is then plotted against potential, and slopes of the plot are measured.

A generalized plot of data obtained from such testing is shown in figure 1. The cathodic or lower portion of the curve represents electrochemical reduction reactions at the surface of the metal. These reactions are typically reduction of oxygen or hydrogen ions. The anodic or upper portion of the curve represents oxidation of the metal, which is the cause of corrosion. A relatively horizontal anodic curve indicates rapid corrosion. A vertical line suggests passivation in which corrosion of metal is inhibited by unreactive layers forming on the metal surface.

At the point where the reduction and oxidation reaction rates are balanced, the test equipment registers no current flow. This "zero current potential" is commonly referred to as the corrosion potential (E_{corr}) or open circuit potential. This potential varies depending on the composition and history of the metal, solution composition, and the conditions under which the corrosion test is performed. Ferrous alloys in aqueous solutions generally have corrosion potentials of -400 mV or lower when measured against a calomel reference. Potentials more positive than this value indicate possible passivation or inhibited corrosion of the metal.

Corrosion rates in this study were determined using the polarization resistance equation to calculate the corrosion current:

$$i = \frac{(\beta_a)\ (\beta_c)}{2.303\ R_p\ (\beta_a + \beta_c)},$$

where i = corrosion current,

R_p = polarization resistance,

β_c = cathodic Tafel slope,

and β_a = anodic Tafel slope.

A more extensive discussion is presented by Dean (5).

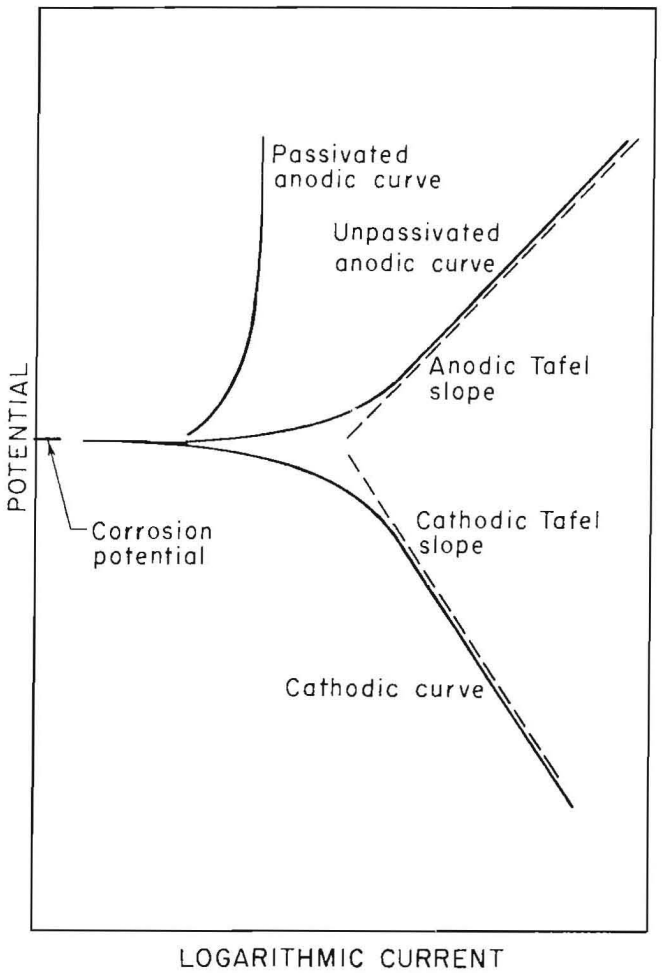

FIGURE 1. - Generalized potentiodynamic plot of corrosion data.

EXPERIMENTAL METHODS

SAMPLES

Eight types of ferrous grinding media were obtained from different suppliers. These included both cast and forged media. These media were analyzed for metallic alloying elements by X-ray fluorescence. Samples of each material were annealed and machined to produce chips for carbon analyses. Chemical analyses of the media are given in table 1.

For this test program, three or four pieces of each type of medium were tested at least twice to obtain averages and deviations of corrosion data.

Media 1 and 2 were forged balls of 1-in and 1-1/2-in diam, respectively. These balls contained small amounts of manganese and silica along with traces of copper, chromium, and nickel. The average surface hardness was Rockwell C 61.

Medium 3 was 2-in cast balls of generally the same composition as the first two media. Average surface hardness of these balls was Rockwell C 64. The balls typically contained several large voids. Silica inclusions were very obvious on polished sections during metallographic examinations.

Medium 4 was nominally an AISI 4130 alloy and was chosen to be representative of material used in mill liners. This sample was in the form of rolled sheet approximately 1.9 cm thick with a uniform hardness of Rockwell C 24 throughout the cross section. Corrosion rates were measured on a polished cross section perpendicular to the direction of rolling.

TABLE 1. - Chemical analyses of grinding media, weight percent (balance Fe)

Medium	C	Mn	Cr	Ni	Cu	Mo
1—Forged steel	0.61	0.56	0.12	0.08	0.22	0
2—Forged steel	.70	.63	.45	.1	.27	0
3—Cast steel	.79	.67	.23	.1	.27	0
4—AISI 4130	.31	.54	1.12	.07	.1	.2
5—Ni-Hard	3.03	.43	1.6	3.0	.15	.14
6—22 pct Cr	3.0	.05	22	.25	.12	0
7—29 pct Cr	2.8	.05	29	.25	.09	0
8—31 pct Cr	2.35	.1	31	.21	.05	0

Medium 5 was cast, 1-in-diam, Ni-Hard balls. Surface hardness of these balls was Rockwell C 60. Metallographic examination of etched sections of these balls showed dendritic structure around the edges of the castings.

Medium 6 was cast, 1-in-diam, 22-pct-Cr balls. Small amounts of manganese, nickel, and copper were also present. These had a surface hardness of Rockwell C 63.

Medium 7 was cast, 1-in-diam, 29-pct-Cr white iron balls. These balls contained small amounts of manganese, nickel, and copper. Surface hardness was Rockwell C 60.

Medium 8 was cast, 1-1/2-in-diam, 31-pct-Cr balls. These balls contained small amounts of manganese, nickel, and copper. Surface hardness for these balls was Rockwell C 56.

TEST SOLUTION

Compounds used in preparing synthetic mill solutions are shown in table 2. This composition was determined from solution analysis obtained from commercial grinding circuits.

TABLE 2. - Synthetic mill solution materials

Salt	Conc, g/L
NaCl	2.17
KCl	.15
$MgCl_2 \cdot 6H_2O$	1.09
$CaSO_4 \cdot 1/2H_2O$	1.01
Na_2SiO_3	.02

EQUIPMENT

The test apparatus was a 1-L flask as shown in figures 2 and 3. An epoxy-mounted test piece was suspended in the center of the flask by a steel rod. The steel support rod was covered by latex tubing to avoid any contact with the solution, which could influence the corrosion measurements.

The support rod for the test specimen was attached to a 300-W ultrasonic probe to provide grinding action at the test surface during corrosion measurement. Ultrasonics simulated the scouring action of a grinding mill while the test piece was held stationary. To ensure electrical isolation of the test piece from the ultrasonic probe, an insulating washer was installed between the rod and probe.

Electrochemical corrosion measurements were made with a scanning potentiostat. A standard calomel electrode, connected by a capillary salt bridge, was used for reference. Two graphite rods spaced on either side of the test specimen acted as inert counter electrodes. The system was sparged with moist air during testing to maintain oxygen levels in solution. A magnetic stirrer provided mild agitation during the corrosion tests.

PROCEDURE

Sample Preparation

Before mounting and polishing, test specimens were cleaned with organic solvents to remove organic materials on the metal surfaces and with strong acids to remove the corrosion products. Flat faces to be used for test surfaces were ground on the balls. The samples were then cast in epoxy. The casting was drilled and tapped so that the specimen could be suspended rigidly in the corrosion flask from a threaded rod. The test piece was suspended so that the test surface was vertical, and electrical contact was made through the support rod.

Immediately before each test scan, the face of the test piece was polished with emery cloth, lapped with 0.05-μm-diam alumina, rinsed with distilled water, and dried with a clean tissue. The diameter of the exposed surface was measured with calipers to calculate surface area.

The polished test piece was positioned in the empty corrosion flask to assure that the reference electrode was adjacent to the center of the test surface. Five grams of powdered calcium carbonate, which is virtually insoluble in the test solution, was added to buffer the pH at 8.3. Five grams of alumina powder, which is commonly used as an abrasive in metal finishing, was added to aid in scouring the test surface during corrosion testing.

After the electrodes had been positioned in the flask and the potentiostat had been connected, a 900-mL aliquot of the test solution was poured into the flask. The corrosion scan was started immediately to reduce the possibility of corrosion layers on the test surface. Ultrasonic abrasion of the surface was also started at the beginning of the test and maintained at the maximum power output of the instrument throughout the entire test. Solution temperature was maintained at 22° C during these tests.

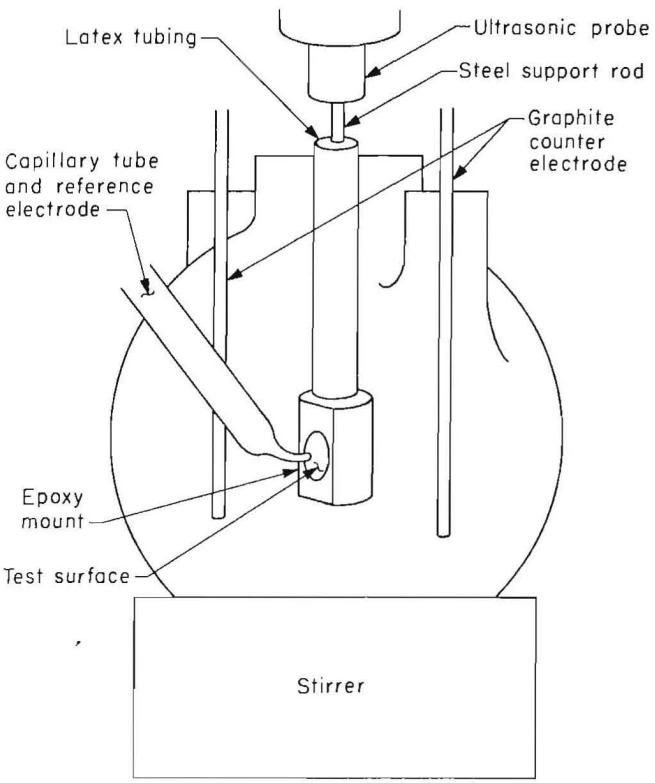

FIGURE 2. - Schematic diagram of electrochemical test apparatus showing corrosion test cell, test sample, and ultrasonic probe to measure corrosion rates of grinding media under simulated grinding conditions.

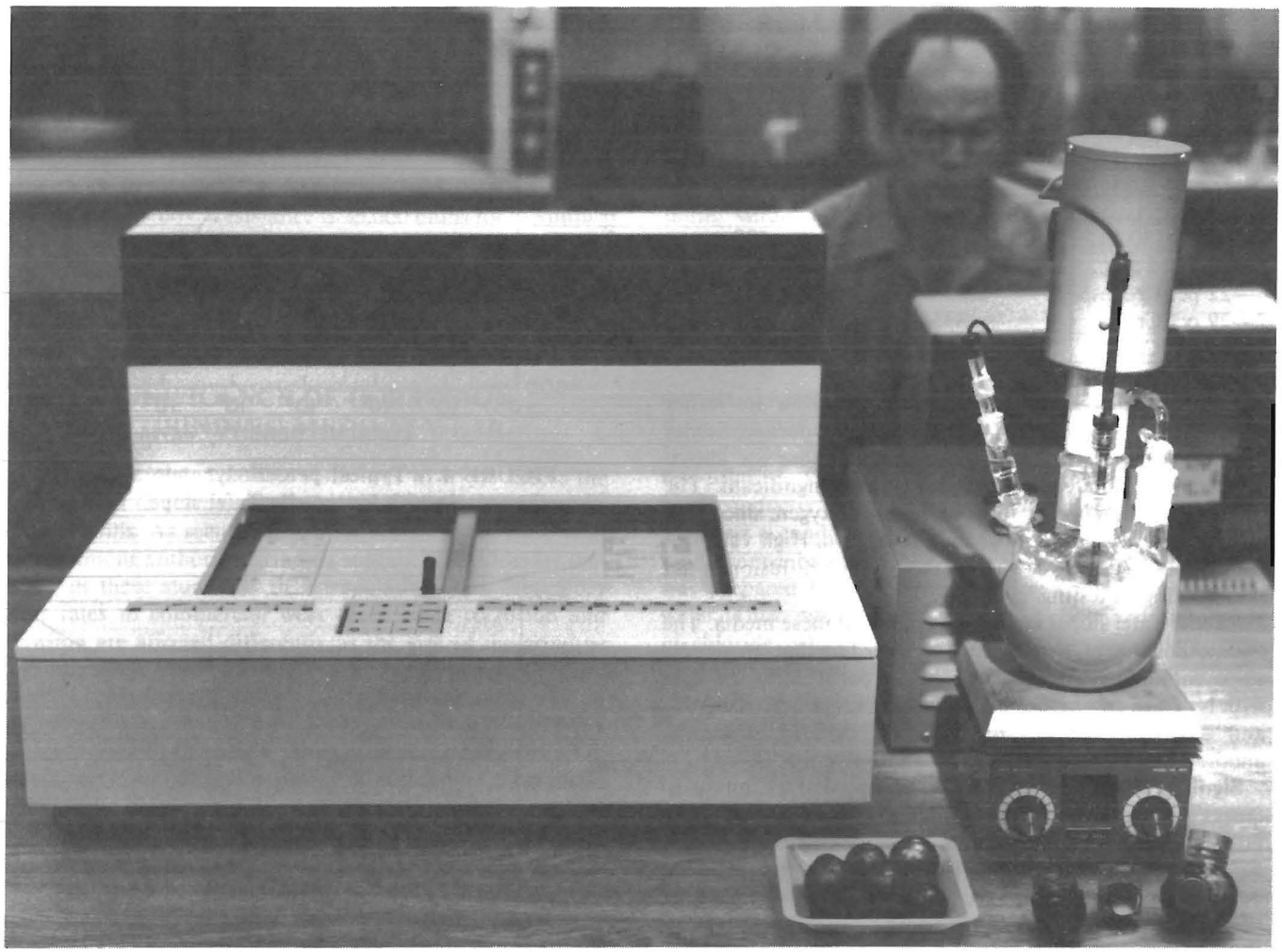

FIGURE 3. - Electrochemical corrosion test apparatus with ultrasonic probe to simulate grinding.

Test Operation

Corrosion data were collected as polarization resistance scans. Scanning was started at a potential 150 mV below the rest potential of the specimen and terminated at 150 mV above the rest potential. Scan rate was 0.2 mV/s. Tafel slopes and polarization resistances were determined graphically from plots of the data.

Cathodic Tafel slopes were measured between approximately 50 and 100 mV below the corrosion potential. Anodic Tafel slopes were determined at approximately 30 to 50 mV above the corrosion potential. Polarization resistances were calculated by linear regression from -20 mV to +20 mV relative to the corrosion potential. Corrosion rates were calculated from polarization results. Because the solutions were highly conductive, no correction was made for solution resistance in determining polarization resistances.

After corrosion tests, test specimens were examined under the electron microscope for pitting and other nonuniform types of corrosion. Chemical composition of materials left on corroded surfaces was also determined by electron microscopy using X-rays.

RESULTS

CORROSION RATE DATA

Average corrosion potentials and corrosion rates for the eight media are reported in table 3. Complete corrosion data for tests performed during this study are tabulated in appendix A. In the discussion, data are grouped into three categories according to chromium content of the media.

Low-Chromium Alloys

The shapes of potentiodynamic curves for medium-carbon steels (media 1, 2, and 3) and the low-chromium alloys (media 4 and 5) are virtually identical. The typical potentiodynamic curve in figure 4 indicates these materials do not passivate.

TABLE 3. - Average corrosion rates and corrosion potentials of grinding media tested in this study

Medium	Corrosion rate, mpy	Corrosion potential, mV
1—Forged steel ..	9.82	-452
2—Forged steel ..	8.63	-437
3—Cast steel	8.80	-463
4—AISI 4130	4.65	-430
5—Ni-Hard	4.42	-379
6—22 pct Cr	2.05	-360
7—29 pct Cr	.335	-292
8—31 pct Cr	.141	-264

Cathodic Tafel slopes for all of these media are rather high, ranging between 0.16 and about 0.2 V/decade. Slopes for carbon steels tend to be higher than those for alloys, although the difference is not statistically significant. The cathodic reaction is probably reduction of oxygen, since high pH would minimize hydrogen ion reduction. High values of the cathodic Tafel slope suggest that oxygen diffusion is not rate limiting in testing.

Anodic Tafel slopes are very small for all these media. The anodic portion of several curves is so flat that an anodic slope cannot be determined. This is particularly the case with Ni-Hard specimens. Anodic slopes range between 0.026 and 0.034 V/decade. No significant differences among anodic Tafel slopes are found for these five media.

Significant differences are found in polarization resistances among these media. Carbon steel media have a low polarization resistance of about 600 ohms. Differences between cast and forged media are insignificant. A value of 1,340 ohms for Ni-Hard is the highest polarization resistance of all five materials. Because of significantly higher polarization resistances of the alloys compared with carbon steels, the corrosion rates are about half that of carbon steels. Carbon steel media have a corrosion rate of about 9 mpy compared with about 4.5 for 4130 and Ni-Hard alloys.

22-pct-Cr Alloy

Potentiodynamic curves for 22-pct-Cr alloy (medium 6), shown in figure 5, resemble those of low-chromium alloys. No passivation of this alloy was found in this test solution. The cathodic Tafel slope is 0.136 V/decade, which is lower than that of media 1-5. The anodic slope of 0.036 V/decade is equivalent to that of media 1-5; however, the polarization resistance of 2,920 ohms is significantly greater than the values for media 1-5. This higher resistance indicates a corrosion rate of 2.05 mpy for medium 6.

High-Chromium Alloys

A potentiodynamic plot typical of the curves for high-chromium alloys (media 7 and 8) is shown in figure 6. This plot shows passivation of these media occurs during anodic polarization. Cathodic Tafel slopes are 0.095 to 0.098 V/decade, which are lower than values measured for other media. Anodic slopes for these media are difficult to determine. The slope for medium 7 appears to be about 0.12 V/decade. The anodic slope for medium 8 cannot be determined graphically owing to absence of a linear portion of the

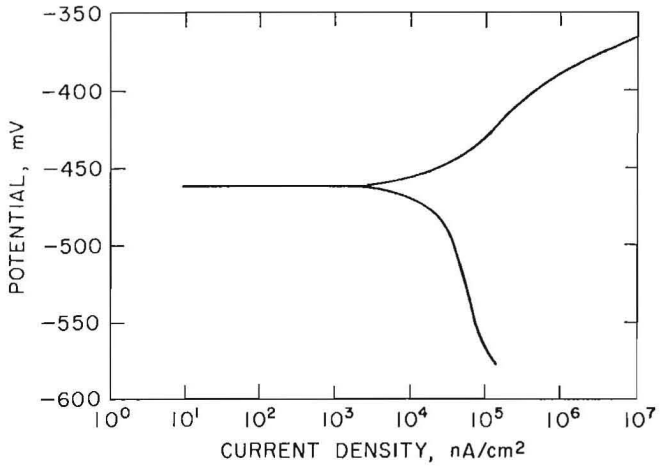

FIGURE 4. - Typical potentiodynamic plot for low-chromium steels with low anodic Tafel slope.

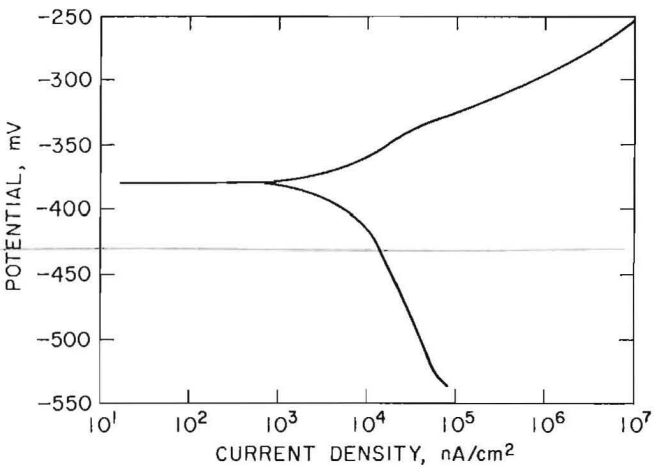

FIGURE 5. - Potentiodynamic plot typical of 22-pct-Cr white irons.

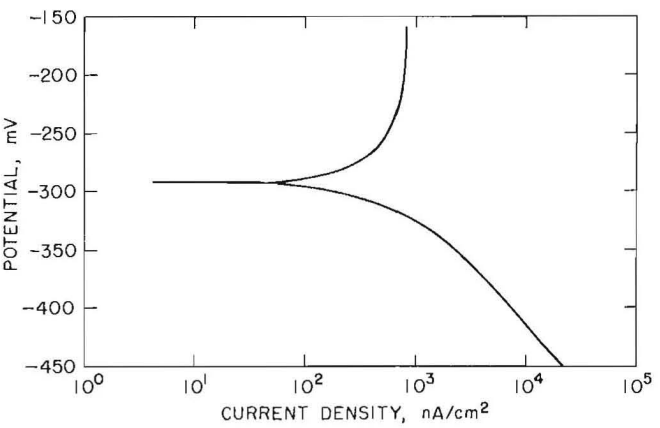

FIGURE 6. - Potentiodynamic plot typical of high-chromium white irons showing passivation during anodic sweep.

anodic curve and is therefore arbitrarily assigned the value of 0.1. This value is roughly equivalent to the value of 0.12 measured for the 29-pct-Cr medium, and deviations as large as 30 pct in the Tafel slope will not affect the calculation of the corrosion rate by more than 10 pct.

Polarization resistances increase by more than an order of magnitude for media 7 and 8 compared with the other media tested in this study. Resistance is 36,000 ohms for medium 7 and 70,000 for medium 8. These resistances correspond to corrosion rates of 0.34 and 0.14 mpy, respectively.

CORROSION POTENTIALS

Corrosion potentials of metals increased significantly as chromium content increased. Carbon steels have corrosion potentials of about -0.45 V versus SCE as measured during potentiodynamic scanning. This low value of the potential indicates uninhibited corrosion. Potentials for high-chromium white irons are between about -0.26 and -0.30 V. These high potentials suggest some passivation despite ultrasonic abrasion during the test.

DISCUSSION

SIGNIFICANCE OF CORROSION IN GRINDING MEDIUM WEAR

An important goal of this study was to try to assess the contribution of corrosion to grinding medium wear in commercial mills. As seen in the introduction, there is no consensus among authors of grinding studies. One difficulty that arises in these studies is in extrapolating from laboratory wear rates to commercial wear rates, since corrosion and abrasion are affected differently as the size of the grinding mill increases. Corrosion rates in mills of various sizes are directly comparable if reported in penetration rates such as micrometers per hour or mils per year. Hence, corrosion rates reported in this study should give a good indication of actual corrosion rates in commercial mills. While corrosion rates should be comparable, Norman (15) reported that abrasive wear increases in a nonlinear way as mill size increases, suggesting that corrosion accounts for a smaller fraction of total wear as mill size increases.

Corrosion rates measured on media 1 and 2, typical of about 80 pct of the grinding media consumed (12), are approximately 9 mpy. Recently Norman (15) published data on wear rates in commercial comminution equipment and reported typical values for rods, balls, and liners from 4 μm/h (1,380 mpy) to 30 μm/h (10,300 mpy), or approximately 15 μm/h (5,200 mpy) as an average value.

Natarajan (14) found a maximum corrosion rate of approximately 0.23 μm/h (80 mpy), or approximately 1.5 pct of the wear rate typical in commercial grinding mills. Lui (10) reported the corrosion rate of steel grinding media in laboratory mills to be 0.4 mg/cm^2•h (176 mpy), or about 3.5 pct of the wear typical of commercial mills. Corrosion rates of about 10 mpy measured in this research indicate that somewhat less than 1 pct of typical wear is due to corrosion.

Bond (1) suggested that corrosion is primarily responsible for increased wear in wet grinding compared to dry grinding. Based on the above discussion, other reasons for increased wear in wet milling as opposed to dry milling must be considered. A likely explanation is that the increased grinding rate known to accompany wet milling also dramatically increases the abrasive wear rate of media.

TEST SOLUTION

One objective of this study was to compare corrosion rates of common grinding media in a solution typical of those encountered in wet grinding. To relate the data to operating circuits, the test solution was chosen to match mill solutions from commercial milling operations. In all aqueous corrosion studies, the corrosion rate is highly dependent on the test solution. Remark (16) found mill solutions commonly have conductivities of 0.09 to 6.0 mmho/cm. Our test solution had a conductivity of 5.1 mmho/cm, which is higher than average based on data from Remark. The test solution was prepared to match the chemical composition of mill water. Thus, our synthetic mill water contained high levels of chloride, which is known to mediate particularly high corrosion rates, as shown by LeGault (9). Corrosion rates measured in this study could, therefore, be expected to be higher than average for media in typical grinding circuits.

COMPARISON OF CORROSION RATES

Data in table 3 show that the corrosion rate of cast media is equivalent to the corrosion rate of forged media of the same composition and hardness. The Tafel slopes and the shape of the potentiodynamic plot are also equivalent; hence, corrosion characteristics of cast and forged media are equivalent in this system.

The data show a statistically significant decrease in corrosion rate as the chromium content of the steel increases. Carbon steel media have corrosion rates of about 9 mpy. Low-chromium alloys (media 4 and 5) have corrosion rates of about 4.5 mpy, which is half that of carbon steels.

The 22-pct-Cr medium has a corrosion rate of about 2 mpy, which is about 50 pct of that for low-chrome alloys.

To show the beneficial effects of chromium on corrosion, corrosion rates are plotted against the chromium content of metal (fig. 7). The decrease in rate for white irons (media 4 through 8) appears to be nearly linear with chromium content.

Another factor that appears to contribute to medium corrosion is sulfide inclusions. Examination of test pieces under the electron microscope showed that sulfide inclusions are more common in carbon steels than in white irons. The photomicrograph in figure 8 shows the corroded surface of a carbon steel piece. Corrosion has caused a large pit to form on the surface of the test specimen. Protruding from this corrosion pit is an inclusion composed primarily of manganese, iron, and sulfur. This composition is typical of sulfide inclusions seen in these steels. These inclusions usually contain sulfur and manganese as major components. Iron is always present in various amounts. Nickel and copper were also seen in some inclusions. The rodlike shape and smooth

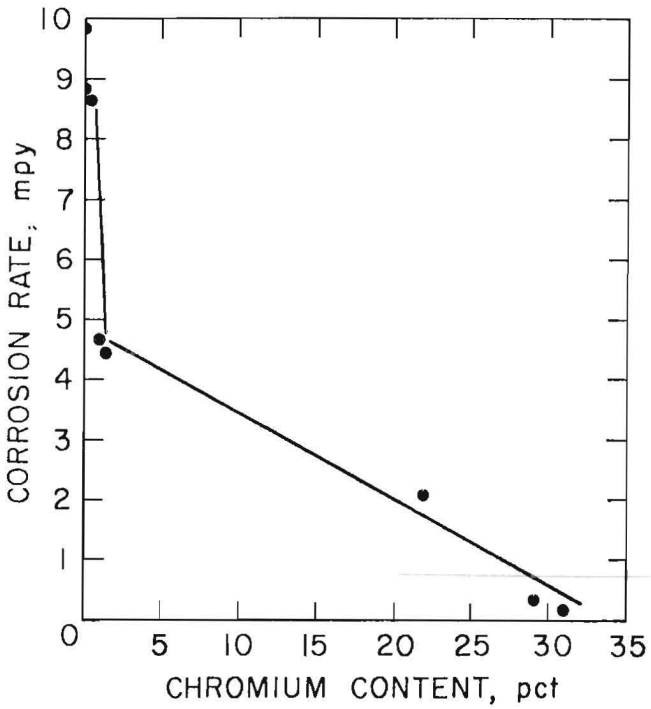

FIGURE 7. - Corrosion rate as a function of chromium content of steel.

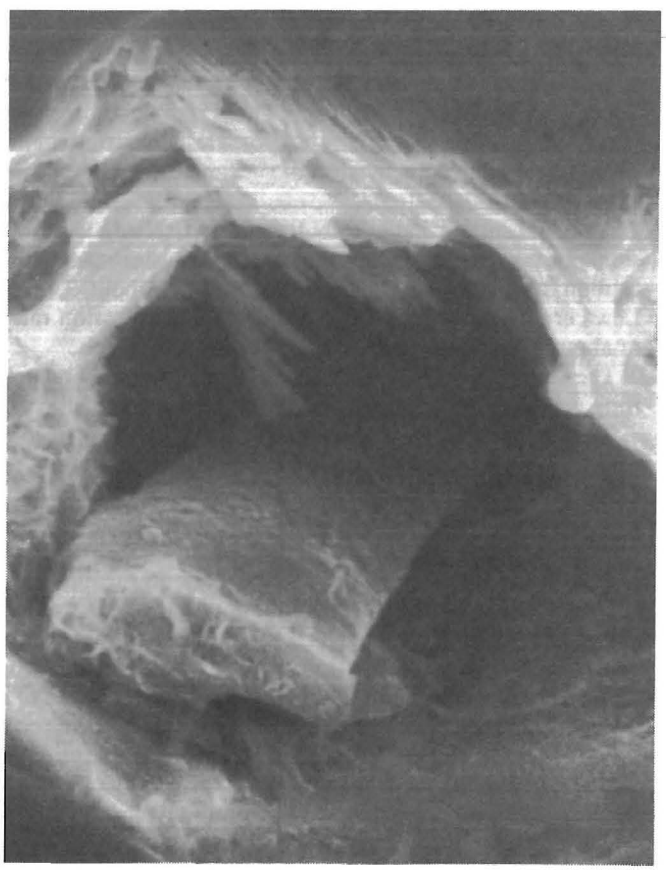

FIGURE 8. - Photomicrograph of sulfide inclusion on corroded metal surface.

sides of this inclusion are also typical. Polished ends where inclusions had originally intersected the surface were also visible even after corrosion testing.

These inclusions were generally found in pits on corroded surfaces and occurred in great numbers in media 1, 2, and 3. Remaining media contained few sulfide inclusions, and there appeared to be less tendency to form large pits around inclusions during corrosion of these media.

Because inclusions in these media appear relatively intact after corrosion, it is suspected that the inclusions act as cathodes promoting galvanic corrosion of the metal. Galvanic action causes rapid dissolution of the metal immediately surrounding the inclusion, thereby forming the pit. Early research by Cobb (3) showed that galvanic reactions do occur between sulfur inclusions and steel.

This pitting should be distinguished from pitting corrosion, where the passivation layer fails in localized areas, resulting in pit formation. The pitting discussed here appears to result from localized galvanic corrosion between the alloy and electroactive inclusions.

Siliceous inclusions are frequent in media 1, 2, and 3. Separate phases containing silicate materials were not seen in media 4-8.

CORROSION POTENTIALS

Figure 9 shows the relationship between corrosion potential and chromium content of the metal to be approximately linear. Despite evidence of passivation for some of the higher chromium alloys, a significant point about these corrosion potentials is that they are lower (more electrochemically "active") than open circuit potentials of common semiconducting minerals. This difference in potentials between metal and minerals indicates that galvanic corrosion of metals will occur in the grinding mill. Hoey (8), for example, reports higher medium corrosion when grinding sulfide ores compared with grinding hematite ores. The rates are 1 mg/cm^2•h (440 mpy) and 0.4 mg/cm^2•h (176 mpy), respectively.

The possibility of sulfide minerals acting as electrodes has been recognized for many years and has been reviewed by

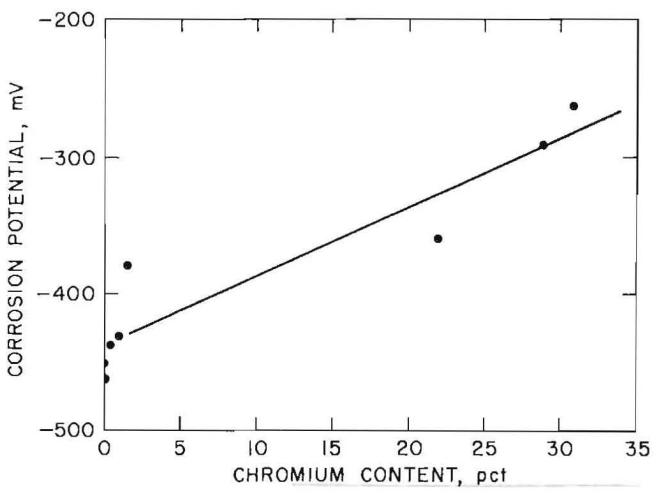

FIGURE 9. - Corrosion potentials as a function of chromium content of ferrous alloys.

Shuey (19) and Sato (17). Natarajan reported that practical electrochemical potentials for most sulfide minerals are approximately 0 V versus SCE because of kinetic factors (13). Hiskey (7) and the Bureau of Mines (18) have shown that various metals, including iron, can act as reductants for sulfide minerals. Although galvanic corrosion during grinding is possible, data are insufficient to predict the magnitude of this type of corrosion in a grinding system. Remark (16) predicted that galvanic corrosion in the presence of minerals, which he assumed to have a surface area approximately 1,000 times larger than the steel, could account for as much as 90 pct of the wear in grinding mills. A calculation to estimate the surface area ratio of minerals to grinding media is shown in appendix B and indicates that the ratio is more nearly 5, which would greatly reduce the galvanic corrosion rate predicted by Remark.

SUMMARY AND CONCLUSIONS

This report presents data on the corrosion rates of common grinding medium alloys in typical mill water. Since abrasion is known to stimulate corrosion, ultrasonic grinding of the media was used during the corrosion tests to simulate the scouring action of the ore pulp. The corrosion rates calculated from electrochemical measurements ranged between 0.1 and 10 mpy, depending on the amount of chromium and the number of inclusions in the alloy. These corrosion rates were compared with typical wear rates in commercial grinding mills, which are about 5,200 mpy. Discussion of the data suggested the following conclusions:

1. Corrosion rates of 0.1 to 10 mpy were measured for common grinding alloys in synthetic mill water under abrasive conditions.

2. Literature reports indicate 5,200 mpy is typical for wear rates in commercial grinding mills. The literature also indicates that corrosion control methods can reduce wear rates by 400 mpy in systems where corrosion is enhanced by severe abrasion. Based on these data, it seems unlikely that corrosion, even when accelerated by rapid abrasion, can be responsible for more than 5 to 10 pct of the wear in *typical* commercial grinding mills.

3. Based on the corrosion potentials measured during this study, galvanic corrosion can be expected to occur between grinding media and ores containing semiconducting minerals. Insufficient data are available to assess the magnitude of galvanic corrosion in grinding. This is an area that deserves further research.

4. As would be expected, the addition of chromium as an alloying element in grinding media decreases the corrosion rate. Qualitative data suggest that sulfidic inclusions in the steel, particularly in the low-alloy steels, may contribute to corrosion of the media.

A major deficiency in grinding medium corrosion research is the absence of reliable data characterizing the surface of media during mill operation. Before better measurements of corrosion rates can be made, considerable progress must be made in measuring the extent of medium passivation during grinding. The present study did not consider the effects of minerals, dissolved oxygen, corrosion inhibitors, or grinding efficiency (i.e., intensity of the abrasion in grinding). A study of these parameters would give much valuable information about corrosion in grinding systems and should be included in future research on this topic.

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APPENDIX A.—CORROSION DATA

TABLE A-1. - Corrosion data, medium 1

E_{corr}, V	Tafel slope, V/decade		Polarization resistance, ohms	Corrosion rate, mpy
	Cathodic	Anodic		
-0.439	0.240	0.033	327.2	17.80
-.448	.194	.022	837.7	4.49
-.442	.170	.036	789.4	7.54
-.464	.162	.029	597.1	8.25
-.427	.161	.031	915.6	5.69
-.443	.198	.023	555.0	7.44
-.413	.191	.027	698.8	6.78
-.440	.203	.018	699.5	4.74
-.550	.242	.050	416.6	20.00
-.461	.172	.045	580.2	12.40
-.451	.115	.034	248.0	4.20
-.456	.165	.044	595.7	11.70
-.454	.113	.041	572.0	3.87
-.446	.236	.044	330.8	22.60
AVERAGES				
-0.452	0.183	0.034	726.0	9.82
ESTIMATED STANDARD DEVIATIONS				
0.031	0.040	9.7×10^{-3}	343.9	6.21

TABLE A-2. - Corrosion data, medium 2

E_{corr}, V	Tafel slope, V/decade		Polarization resistance, ohms	Corrosion rate, mpy
	Cathodic	Anodic		
-0.426	0.239	0.024	367.8	11.80
-.427	.181	.030	1,410.0	3.65
-.440	.193	.020	707.7	5.04
-.448	.260	.028	826.5	6.13
-.439	.147	.023	338.9	11.80
-.439	.191	.031	398.4	13.40
AVERAGES				
-0.437	0.202	0.026	674.9	8.63
ESTIMATED STANDARD DEVIATIONS				
8.45×10^{-3}	0.040	4.33×10^{-3}	411.8	4.16

TABLE A-3. - Corrosion data, medium 3

E_{corr}, V	Tafel slope, V/decade		Polarization resistance, ohms	Corrosion rate, mpy
	Cathodic	Anodic		
-0.452	0.223	0.026	885.0	5.27
-.470	.153	.025	421.0	10.20
-.451	.157	.025	466.0	9.28
-.441	.171	.029	504.0	9.84
-.475	.163	.030	536.0	9.48
-.489	.184	.030	599.0	8.62
-.462	.171	.033	620.0	8.94
AVERAGES				
-0.463	0.175	0.028	575.9	8.80
ESTIMATED STANDARD DEVIATIONS				
0.016	0.023	3.03×10^{-3}	153.2	1.64

TABLE A-4. - Corrosion data, medium 4

E_{corr}, V	Tafel slope, V/decade		Polarization resistance, ohms	Corrosion rate, mpy
	Cathodic	Anodic		
-0.451	0.175	0.033	1,138.0	4.89
-.433	.211	.022	1,413.0	2.83
-.456	.189	.031	834.7	6.39
-.420	.197	.019	1,035.0	3.35
-.441	.162	.026	1,405.0	3.20
-.452	.223	.032	966.2	5.80
-.390	.201	.027	1,108.0	4.31
-.394	.161	.027	585.9	6.45
AVERAGES				
-0.430	0.190	0.027	1,060.7	4.65
ESTIMATED STANDARD DEVIATIONS				
0.025	0.022	4.88×10^{-3}	277.0	1.45

TABLE A-5. - Corrosion data, medium 5

E_{corr}, V	Tafel slope, V/decade		Polarization resistance, ohms	Corrosion rate, mpy
	Cathodic	Anodic		
-0.400	0.199	0.056	924.4	9.42
-.415	.157	.057	1,612.0	6.14
-.356	.163	.017	1,637.0	2.86
-.381	.170	.016	1,470.0	4.07
-.365	.167	.016	1,328.0	4.04
-.373	.184	.032	1,119.0	4.91
-.370	.201	.027	1,414.0	3.35
-.363	.157	.020	886.8	4.01
-.384	.174	.014	955.7	2.73
-.384	.136	.035	2,080.0	2.68
AVERAGES				
-0.379	0.171	0.029	1,342.7	4.42
ESTIMATED STANDARD DEVIATIONS				
0.017	0.019	0.016	381.1	2.05

TABLE A-6. - Corrosion data, medium 6

E_{corr}, V	Tafel slope, V/decade		Polarization resistance, ohms	Corrosion rate, mpy
	Cathodic	Anodic		
-0.360	0.125	0.041	4,370	1.42
-.357	.120	.040	3,783	1.63
-.361	.147	.022	3,552	1.08
-.374	.151	.045	2,347	2.70
-.345	.156	.020	2,994	1.20
-.346	.141	.025	2,548	1.69
-.348	.134	.060	3,050	1.94
-.359	.155	.013	1,386	1.77
-.355	.102	.036	2,378	4.20
-.398	.130	.058	2,782	2.90
AVERAGES				
-0.360	0.136	0.036	2,919	2.05
ESTIMATED STANDARD DEVIATIONS				
0.015	0.017	0.015	843.4	0.955

TABLE A-7. - Corrosion data, medium 7

E_{corr}, V	Tafel slope, V/decade		Polarization resistance, ohms	Corrosion rate, mpy
	Cathodic	Anodic		
-0.292	0.103	0.088	46,370	0.206
-.286	.100	.139	52,990	.220
-.303	.098	.145	28,790	.358
-.297	.113	.088	19,380	.427
-.242	.083	.123	63,410	.160
-.290	.086	.148	28,380	.384
-.309	.094	.124	21,320	.503
-.321	.103	.136	27,990	.419
AVERAGES				
-0.292	0.098	0.124	36,080	0.335
ESTIMATED STANDARD DEVIATIONS				
0.023	9.72×10^{-3}	0.023	16,100	0.123

TABLE A-8. - Corrosion data, medium 8

E_{corr}, V	Tafel slope, V/decade		Polarization resistance, ohms	Corrosion rate, mpy
	Cathodic	Anodic		
-0.256	0.099	ND	65,820	0.152
-.273	.098	ND	60,040	.165
-.265	.090	ND	65,280	.146
-.265	.099	ND	71,850	.139
-.258	.093	ND	81,950	.118
-.267	.086	ND	73,450	.127
AVERAGES				
-0.264	0.095	ND	69,730	0.141
ESTIMATED STANDARD DEVIATIONS				
6.19×10^{-3}	5.18×10^{-3}	ND	7,701	0.017

ND Not determined.

APPENDIX B.—CALCULATION OF SURFACE AREA RATIOS OF MINERALS TO MEDIA

To estimate galvanic corrosion rates according to Wesley's (20) method, it is necessary to know the ratio of cathodic to anodic surface area. In this case, the anodic material is the grinding medium and the cathodic material is the semiconducting mineral. The following assumptions are necessary in this calculation:[1]

1. 35 pct void space in the ball change.

2. Average ball radius (r) = 2.54 cm.

3. Volume percent of ore (v/o) = 34 pct (75 pct pulp density).

4. 5 pct semiconducting mineral in ore.

5. Average particle dimension (D) = 0.015 cm (100 mesh).

6. Cubic mineral particles.

7. N = number of grinding balls per unit of mill volume.

8. M = number of mineral particles per unit of mill volume.

$$N = \frac{(1 - 0.35)}{\frac{4}{3}\pi r^3}$$

Surface area of medium = $4 \pi r^2 N$

$$= 4 \pi r^2 \left[\frac{(1 - 0.35)}{\frac{4}{3}\pi r^3}\right]$$

$$= \frac{0.768 \text{ cm}^2 \text{ medium surface area}}{\text{unit of mill volume}}$$

$$M = \frac{\frac{\text{void space}}{100} \times \frac{\text{v/o}}{100} \times \frac{\text{pct mineral in ore}}{100}}{D^3}$$

Surface area of mineral = $6 D^2 M$

$$= 6 \times (0.015)^2 \left[\frac{0.35 \times 34 \times 0.05}{(0.015)^3}\right]$$

$$= \frac{2.38 \text{ cm}^2 \text{ mineral surface area}}{\text{unit of mill volume}}$$

$$\text{Surface area ratio} = \frac{2.38}{0.768} = 3.1$$

Surface areas of the mineral and the medium differ by less than a factor of 5 in this case. A ratio greater than 10 [one order of magnitude]seems unlikely in most cases. Although galvanic corrosion is to be expected in grinding mills, these figures do not indicate that galvanic corrosion will become the overriding factor in grinding mill wear as suggested by Remark (16).

[1]These assumptions are made according to the best estimates of the authors to indicate relative magnitude of the surface area ratio. Assumptions may be changed to fit a particular case.